

# Structure and lattice dynamics of Jahn-Teller crystal $\text{BiMnO}_3$ : ab initio calculation

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**Abstract.** In this work, ab initio study of crystal structure and phonon spectra of  $\text{BiMnO}_3$  has been performed using density functional theory (DFT) with hybrid DFT/Hartree-Fock functionals in CRYSTAL14 code. Crystal structure parameters, infrared and Raman spectra of  $\text{BiMnO}_3$  have been calculated for magnetic ordered monoclinic C2/c phase. Results are compared with existing experimental data. Our results are in agreement with last x-ray diffraction and optical experiments. Using isotopic substitution method ions involved in vibrations are determined. Calculated charge density maps show the antiferroelectric ordering of dipole moments of  $\text{Bi}^{3+}$ .

## 1. Introduction

Crystal compounds of  $\text{BiMO}_3$  ( $M$  – transition metal ion or Al, Ga, In) range are under investigation because of various physical properties which could be used in electronics [1]. The Jahn-Teller crystal  $\text{BiMnO}_3$  (BMO) is a bismuth-based distorted perovskite oxide like  $\text{BiFeO}_3$ . The trivalent bismuth ion possesses of  $6s^2$  lone-pair electrons [2,3,4,5], which make this ion polarized. The transition-metal ions ( $\text{Mn}^{3+}$  or  $\text{Fe}^{3+}$ ) are magnetic. The dipole moments of  $\text{Bi}^{3+}$  sublattice and the magnetic moment of transition metal sublattice are ordered at low temperatures [1-5,6,7]. This coincidence leads to widely discussed multiferroic properties of these compounds [1-7]. The sublattice of orbitally degenerated  $\text{Mn}^{3+}$  ions adds new properties to the correlation between polarization and magnetic subsystem. Thus, the  $\text{BiFeO}_3$  is an antiferromagnetic crystal with ferroelectric (FE) ordering [5]. The  $\text{BiMnO}_3$  is ferromagnetic (FM) and has no spontaneous polarization in the bulk samples [3, 4]. The FM ordering of  $\text{BiMnO}_3$  is caused by orbital ordering of manganese sublattice due to Jahn-Teller effect [8,9]. Under Curie temperature, the centrosymmetric group C2/c of crystal structure leads to absence of ferroelectricity due to symmetry considerations [2, 3, 9]. An inversion symmetry operation causes an impossibility of FM+FE ordering in this crystal. The temperature and external pressure change the crystal structure to monoclinic and orthorhombic symmetry [3, 4, 10], but they cause no changes of spontaneous polarization in the bulk crystal. The experiments using Raman and infrared spectroscopy confirm these considerations [11]. But the phonon spectra are still not investigated in detail due to problems related to very low symmetry of the crystal in magnetic ordered phase. The  $\text{Bi}^{3+}$  dipole moments ordering is studied only in cases FM+FE ordering. The authors have studied the thin films [7] or considered magnetic symmetry breaking [12,13]. The presence of dipole moments is not yet studied neither theoretically nor experimentally.



The current investigation is devoted to *ab initio* calculations of BiMnO<sub>3</sub> crystal structure and optical spectra. We perform a detailed investigation of phonon spectra for the first time and describe the experimental data [11].

## 2. Computational Details

Calculations have been performed in program package CRYSTAL14 [14], within the framework of density functional theory (DFT) using linear combination of atomic orbitals (LCAO) approximation. Hybrid DFT/HF functional WC1LYP has been used with 16% of Hartree-Fock exchange energy. In this functional, the DFT-exchange part is calculated using Wu-Cohen method in generalized gradient approximation (GGA). It should be noted that this functional developed without the fitting parameters. The correlations are taken into account by the functional LYP. All-electron Gauss-type basis sets are used for description of Mn<sup>3+</sup> and O<sup>2-</sup> ions, 86-411d41G and 8-411d1, correspondingly [15]. Heavy Bi<sup>3+</sup> ion is described by Hay-Wadt effective small-core pseudopotential that is taken from a source [16]. External 6s<sup>2</sup> orbital of Bi<sup>3+</sup> ion plays an important role in the formation of the distortion of the crystal lattice, so it is taken into account directly and was not included in the core. All calculations performed in spin-polarized mode in high-spin state S=2 for Mn<sup>3+</sup>. The accuracy of calculations is determined by a set of tolerances for the overlap of wave functions, above which the Coulomb and exchange integrals are calculated. In this paper, the tolerance is selected to be 10<sup>-10</sup> for Coulomb and 10<sup>-20</sup> for the exchange integrals. The integration in reciprocal space is made with 4 x 4 x 4 grid using Monkhorst-Pack scheme. The energy per unit cell is calculated with an accuracy of 10<sup>-8</sup> Hartree.

Phonon frequencies are calculated in the center of first Brillouin zone in harmonic approximation.

## 3. Results and Discussion

### 3.1. Crystal structure

The calculation of crystal structure parameters of BiMnO<sub>3</sub> has been made for monoclinic phase, C2/c space group, in ferromagnetic arrangement of spins. According to x-ray diffraction experiment, that performed for BiMnO<sub>3</sub> single crystal in magnetic ordered state, at T < T<sub>c</sub> there is a center of symmetry and monoclinic C2/c structure is realized, instead of the C2, as previously assumed [17]. The results of our calculation (table 1) are in a good agreement with the experiment [18] (the difference is less than 1%).

**Table 1.** Calculated and experimental [18] (in brackets) crystal structure parameters of BiMnO<sub>3</sub>

Lattice constant	a	b	c	β
Value, Å	9.484(9.569)	5.589(5.602)	9.799(9.879)	110.96(111.02)
Atom coordinates in cell				
Atom	Wyckoff symbol	x/a	y/b	z/c
Bi	8f	0.1351(0.1365)	-0.230(-0.217)	0.1181(0.1269)
Mn1	4e	0	0.2014(0.2113)	0.25
Mn2	4c	0.25	0.25	0
O1	8f	0.0993(0.0991)	0.1666(0.1776)	0.0794(0.0815)
O2	8f	0.3510(0.3524)	0.4496(0.4567)	0.1662(0.1646)
O3	8f	0.1447(0.1443)	0.4161(0.4342)	0.3782(0.3639)
Bond lengths, Å				
Mn1-O1	2.20(2.20)	Mn2-O1	1.91(1.93)	
Mn1-O2	1.91(1.90)	Mn2-O2	2.24(2.23)	
Mn1-O3	1.95(1.97)	Mn2-O3	1.92(1.95)	

### 3.2. Phonon spectra

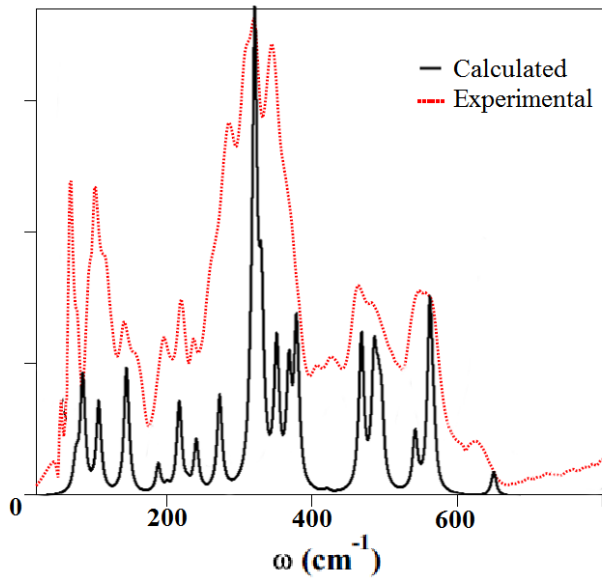
The set of fundamental vibrations in gamma point of BiMnO<sub>3</sub>, in monoclinic C2/c phase, looks as follows:

$$\Gamma = (13A_g + 14B_g)^{Ram} + (14A_u + 16B_u)^{IR} + (A_u + 2B_u)^{Acoust} \quad (1)$$

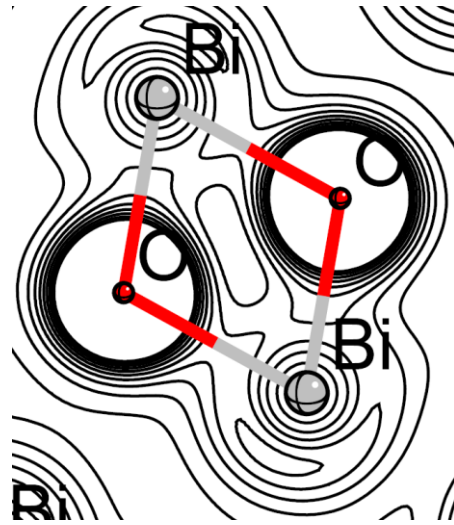
**Table 2.** Irreducible representations, frequencies of IR and Raman modes in cm<sup>-1</sup> and calculated intensities in IR spectrum in a.u.

Infrared					Raman			
№	Repr.	Calc.	Exp. [11]	Calc. Intens.	№	Repr.	Calc.	Exp. [11]
5	A <sub>u</sub>	74	68	16	4	A <sub>g</sub>	53	50
6	B <sub>u</sub>	76	75	59	7	B <sub>g</sub>	81	75
8	B <sub>u</sub>	85	92	255	10	B <sub>g</sub>	93	84
9	A <sub>u</sub>	88	101	0.5	11	B <sub>g</sub>	102	93
12	A <sub>u</sub>	107	115	200	13	A <sub>g</sub>	108	99
16	B <sub>u</sub>	145	143	282	14	A <sub>g</sub>	113	
17	A <sub>u</sub>	189	159	64	15	B <sub>g</sub>	137	133
19	B <sub>u</sub>	201	196	14	18	A <sub>g</sub>	196	180
20	B <sub>u</sub>	218	219	200	21	B <sub>g</sub>	223	
22	A <sub>u</sub>	229		11	23	B <sub>g</sub>	232	
24	B <sub>u</sub>	241	237	112	26	A <sub>g</sub>	262	242
25	A <sub>u</sub>	244		2	28	A <sub>g</sub>	287	278
27	B <sub>u</sub>	273	261	213	29	B <sub>g</sub>	287	
30	A <sub>u</sub>	291		1	34	B <sub>g</sub>	346	
31	B <sub>u</sub>	316	284	66	36	A <sub>g</sub>	358	347
32	B <sub>u</sub>	321	308	1000	37	A <sub>g</sub>	360	
33	A <sub>u</sub>	331	321	374	39	B <sub>g</sub>	373	
35	A <sub>u</sub>	351	345	312	42	B <sub>g</sub>	395	
38	B <sub>u</sub>	368	369	249	44	A <sub>g</sub>	422	400
40	B <sub>u</sub>	379		335	45	A <sub>g</sub>	450	424
41	A <sub>u</sub>	381	407	34	46	B <sub>g</sub>	456	440
43	A <sub>u</sub>	421	426	7	47	A <sub>g</sub>	462	
48	B <sub>u</sub>	468	463	341	49	B <sub>g</sub>	482	
50	A <sub>u</sub>	485	486	261	53	A <sub>g</sub>	523	
51	A <sub>u</sub>	490		141	54	B <sub>g</sub>	533	530
52	B <sub>u</sub>	495	508	159	58	B <sub>g</sub>	646	635
55	B <sub>u</sub>	542	541	128	60	A <sub>g</sub>	652	
56	B <sub>u</sub>	562	561	401				
57	A <sub>u</sub>	567	604	87				
59	A <sub>u</sub>	649	628	54				

Among 60 modes, 27 even modes are active in Raman spectrum, 30 odd are active in infrared (IR) spectrum and 3 odd modes are acoustic. Our calculation predicts all the modes, their irreducible representations, a comparison of results with the experiment [11] is presented in table 2. The comparison with experimental data is complicated because not all the lines are identified in the experimental spectra. There are 25 lines in infrared spectrum, which are taken at T=10K, and 15 Raman lines, which are taken at room temperature in backscattering geometry. Both of the experimental spectra are obtained in the unpolarized configuration, so we compare with the results calculated for the powder sample. Also it should be noted that missing lines in experimental IR spectrum are low intensity lines or narrow doublets.



**Figure 1.** Calculated and experimental (T=10K) infrared spectrum



**Figure 2.** Charge density map in plane of two Bi<sup>3+</sup> ions

In CRYSTAL package, the intensity of the modes  $I_p$  in infrared spectrum is computed according to

$$I_p = \frac{\pi N_A}{3 c^2} d_p |\vec{Z}_p|^2, \quad (2)$$

where  $N_A$  is the Avogadro's number,  $c$  is the speed of light,  $d_p$  is the degeneracy of the mode,  $\vec{Z}_p$  is the mass-weighted effective mode Born charge vector. Calculated  $I_p$  for the IR-active modes for BiMnO<sub>3</sub> are presented in table 2.

The infrared absorbance spectrum  $A(\omega)$ , which is shown in figure 1, is calculated using following model:

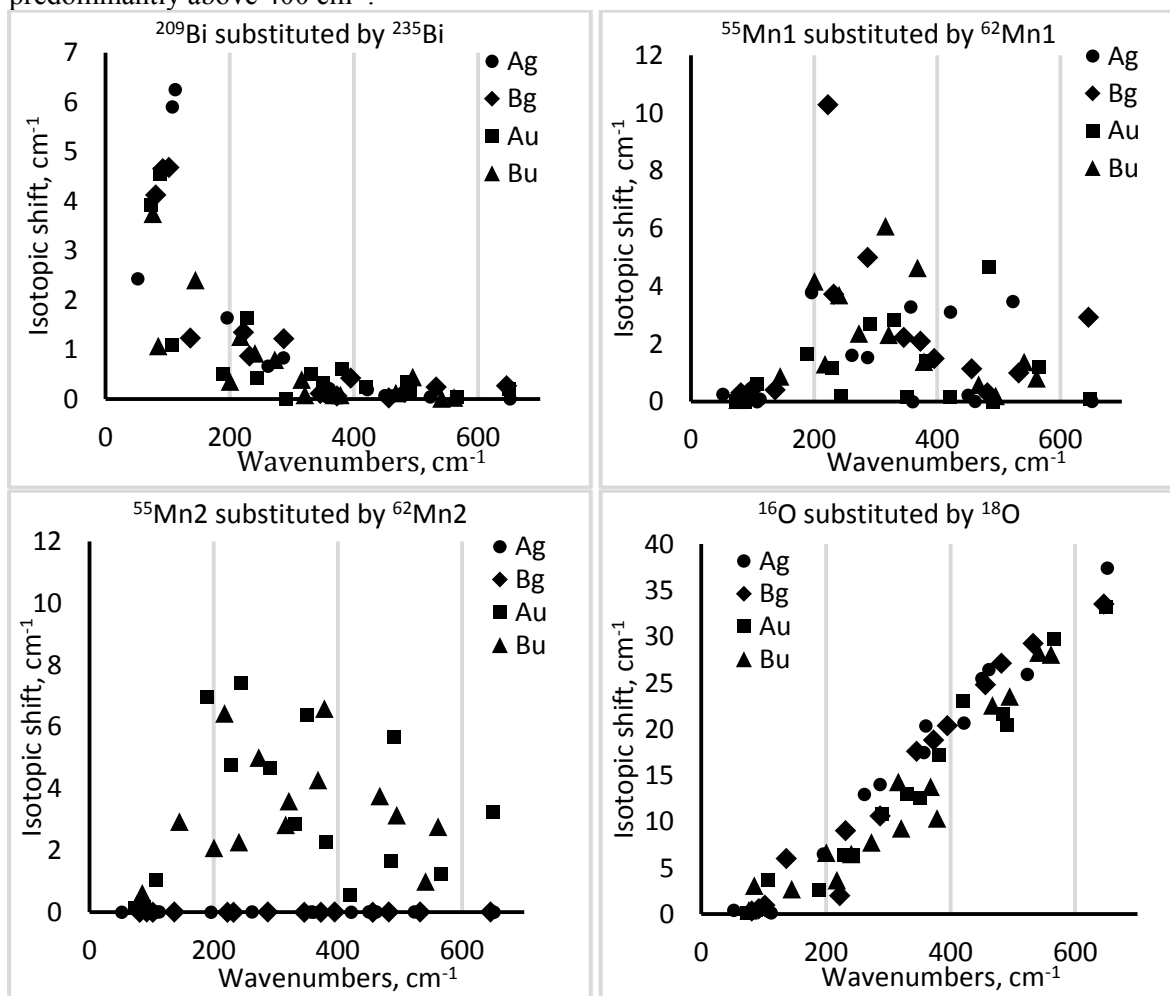
$$A(\omega) = \sum_p \frac{I_p}{\pi} \frac{\gamma_p/2}{(\omega - \omega_p)^2 + \gamma_p^2/4}, \quad (3)$$

where  $\omega_p$  is TO frequency,  $\gamma_p$  is the damping factor ( $\gamma_p=8 \text{ cm}^{-1}$ ), and  $I_p$  is integrated intensity computed as described above.

The phonon frequencies and a IR spectrum which have been obtained in this work are in a good agreement with the existing experimental data [11]. Thereby our results confirm that BiMnO<sub>3</sub> single crystal has centrosymmetric C2/c space group at low temperature.

**3.2.1. Dipole moments.** Using *ab initio* calculations, it is possible to draw a map of charge density in specific plane. Figure 2 shows a charge density around bismuth ions. There is a localization of negative charge near  $\text{Bi}^{3+}$  ion and formation of dipole moment.

**3.2.2. Isotopic substitution.** To determine the ions that take part in vibrations, the isotopic substitution method has been used. The phonon spectrum was recalculated with a changed mass of each symmetrically nonequivalent ion. Obtained frequencies were compared with the initial spectrum and frequency shifts have been determined. In figure 3, results of isotopic substitution are presented. Heavy  $\text{Bi}^{3+}$  ions are involved in vibrations with frequencies below  $200\text{ cm}^{-1}$  approximately. Both positions of manganese ions take part in vibrations in a region of frequencies  $200$  to  $400\text{ cm}^{-1}$ , but Mn2 sublattice is not involved in Raman-active even modes. Oxygen ions take part in all vibrations, predominantly above  $400\text{ cm}^{-1}$ .



**Figure 3.** Isotopic substitution data for  $\text{BiMnO}_3$

#### 4. Conclusion

In this paper, crystal structure parameters of monoclinic centrosymmetric phase of  $\text{BiMnO}_3$  were calculated from first principles. The phonon spectra were calculated and full set of fundamental vibrations, their frequencies and irreducible representations were obtained. Intensities in infrared spectrum were calculated. Despite that the symmetry of the investigated crystal is very low the results obtained are in a good agreement with existing experimental data. The phonon spectra are investigated

using isotopic substitution method. Presence of dipole moments in bismuth sublattice is reproduced in calculations.

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